RESEARCH ON THE PRODUCTION AND PHYSICS OF SINGLE CRYSTAL EMITTERS

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A. Introduction

The transformation of heat directly into useful energy of electrical form, without the usual intermediate inefficient mechanical step, is of military importance in space applications. Research and development efforts have produced the thermionic converter as a promising device for this transformation. Although simple in principle, the production of lightweight, stable, and efficient converters with reproducible electrical characteristics still involves the solution of new and fundamental problems in materials and their vacuum processing. A basic, but at the same time useful, solution to these problems was the aim of this research. Efforts were concentrated on the understanding and improvement of emitter and collector surfaces, since converter performance is very sensitive to these elements. Although not always recognized, this is a processing as well as a materials problem.

Extended surfaces of uniform work function and high temperature stability for long periods of time are the optimum prototype for the theory and development of surfaces which emit and collect electrons in converters. Apparently a single crystal face on a monocrystalline emitter would be the ideal case. Thermionic[1] and field emission[2] experiments indicate to some extent that definite work function assignment might be allowed with respect to crystallographic direction; however, neither theory nor practice

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ABSTRACT

Single crystals of tungsten and molybdenum from 1-10 cm long were produced by the Robison-plus-torsion technique in 4-5 mil filaments. These were studied in an improved electron projection diode, in which point-by-point and average thermionic constants could be measured on the same filament. The work functions for various directions of single crystal molybdenum were found to be the same as those for single crystal tungsten. Also the average values of work function ϕ_R and A_R were 4.40 and 40 respectively, for both tungsten and molybdenum. Thermal treatment always developed facets on the crystal areas of high work function. These facets had highest thermal stability when a shingled structure developed on them during heating.

are able to predict absolute values or to determine what proportionate contributions result from bulk crystalline properties, from the atomic structure of a pure crystallographic plane, or from micropatch structure that can develop preferentially from thermal equilibration,[3] chemical reaction,[4] or from selective adsorption and migration of adatomic species.[5] This work was directed specifically toward these latter aspects of single crystal emitters. Long single crystals were produced in filaments of tungsten and molybdenum, and the thermionic emission from these specimens was studied in a projection diode. This experiment had the advantage that while a number of crystal faces were produced simultaneously each could be studied in detail for the same thermal treatment in the same environment. Each filament as a whole had a well defined and simple patch structure of single crystal faces, so that the effect of patches on the overall emission could be studied with precision. In addition the projection diode method allowed the elastically scattered electrons, a large source of error in most single crystal work, to be measured in a separate experiment.

B. Production of Filamentary Single Crystals

The Robinson technique[6] was used for recrystallization of the highly refractory filaments, with wire sizes of 4-5 mil diameter. Briefly, this method consists in (a) highly polishing the wire by mechanical means,[7] and then (b) heating in high vacuum at a critical annealing temperature until recrystallization is complete. With this technique crystals 1 cm or longer could be grown in tungsten 80% of the time, in thoriated-tungsten 20% of the time, in molybdenum 40% of the time; in a few trial runs, results were negative for W-Mo alloys and rhenium. Twisting about 4 turns per inch[8]

before polishing always produced crystals with a 110-axis aligned within 4^{o} with the wire axis, as determined by X-ray analysis. With the twist technique crystals of 10 cm length were easily produced in tungsten and molybdenum. Only certain specimens of prewar 218-wire could be recrystallized without twisting, and in this case crystals at least 2 cm long with 110-axis deviating by as much as 25^{o} from the wire axis could be obtained. This result was wanted for the later emission studies. The most difficult part of the Robinson technique is to determine the recrystallization temperature, and then to set and hold a prepared filament at this temperature for the necessary annealing time. The best conditions in these experiments were found to be approximately 15 hr at 1900^{o}K for tungsten and thoriated-tungsten, and 15 hr at 1600^{o}K for molybdenum. These temperatures are far below the flash values required to clean up the wires sufficiently to produce surfaces of constant emissivity, necessary for precise optical pyrometry or use of the temperature scales. It is this factor which contributed the most to the relatively low yield of the method.

C. The Projection-diode Technique

In order to arrive at unambiguous information of significance in the physics of emitting materials, one cannot avoid a detailed study of a large number and a variety of crystals, for different treatments and environments. To approach this problem in a quantitative manner, the Johnson-Shockley tube[9] was developed into a precise projection-diode. The description of this tube and its application is given in detail in a separate Air Force Scientific Report.[10] With this method one can

measure the emission constants point-by-point over a single crystal emitter, and coincidently measure the average constants A_R and ϕ_R for the entire emitter in the same tube. Hence, the relative effect of heat treatment on the various patches, or the effect of patches on θ for adsorbed layers can be looked at in a quantitative way.

The essential features of the projection-diode are exhibited in Fig. 1. The construction of the collector is shown in cross section S-S[1]. The pyrex tube wall is B, on which is deposited a conducting film of tin chloride C; a uniform fluorescent screen of zinc sulfide D is placed over this, and the screen is then backed by an opaque aluminum deposit E. The collecting geometry consists of the anode A and two guard rings G, G_2 forming a coaxial system with the single crystal filament F. Figure 2 shows a Richardson plot taken with the tube as a diode; the filament was molybdenum and contained several single crystals within A. Making use of a precise electrometer for emission current measurements, Schottky plots which display both first and second order deviations are obtained. The aluminum-backed fluorescent screen is sensitive enough to allow point-by-point emission measurements to be made by means of a photomultiplier photometer. These results may be obtained in two ways: (a) the rapid scan, illustrated by the photometer trace taken around a single molybdenum crystal and shown in Fig. 3. Trace of this type is important in determining th[illegible]ally equilibrated states of a single crystal either in the clean condition or with adsorbed films. (b) Emission measurements made at various crystallographic directions for various temperatures give the single-direction emission constants. Figure 4 shows

Richardson lines obtained photometrically for the more prominent positions in Fig. 3; associated work functions are recorded. The filament mount is so designed that a good index with emission patterns is maintained for metallography or X-ray analysis on removal from the diode.

D. Thermionic Emission Data

1. Point-by-point Emission Constants.

a. On-axis Tungsten. Work functions measured photometrically for the various directions on a 10-cm W crystal grown by the twist technique, and having its surface accurately in the 110-zone, were no different than those already reported (see Table I, reference 10, pg 3a). Since the correction for electron scattering has not been made at the time of this writing, the [110], [112], and [001] data have the same error as the values given in the table; an estimate of this correction will be given in Section E. However, prolonged heating at 2300°K produced work function minima on the low index directions; this effect will have detailed discussion in Section F.

b. Off-axis Tungsten. A recrystallized filament having the largest deviation from the 110-zone was selected from the group produced by the Robinson method without twist. This 5-mil wire contained two adjacent 2-cm single crystals of good quality, designated A and B, with [110]'s inclined to the wire axis. The wire axis for crystal A corresponded to a <175> crystallographic direction, with the nearest <110> inclined about 12°. Figure 5 is a photometer trace showing variation of emission with orientation for directions perpendicular to the wire axis. Note that the

overall symmetry of this pattern resembles Nichols and Smith,[1] with the deep minima in diametrically opposite < 1710> directions -- the nearest < 110> 's are inclined about 11° to the normals to the wire at these positions. In general that the directions of interest are in a zone which does not contain low index numbers, and atomically smooth patches should not be expected. Work functions measured for the various maxima and minima in Fig. 5 are given in TABLE 1 below. The photometer trace for crystal B is given in Fig. 6. The wire axis for this crystal was the < 251 > direction, with the nearest < 110 > inclined about 25°. Diametrically opposite deep minima appear along a line normal to the wire axis corresponding a < 717 > , but the deviation from the Nichols and Smith symmetry is now large. Note in particular that a minimum corresponding to the < 001 > does not appear. Work functions measured for the various maxima and minima in Fig. 6 are given in TABLE 1 below. Severe heat treatment at 2300°K produced no changes in the emission patterns; metallographic study of the filament revealed that facets with a heavily shingled structure had been produced at the directions corresponding to the deep minima of emission for both crystals. In fact, this shingle structure appeared to be the only outstanding feature common to the surfaces of both crystals.

TABLE 1

Crystal	Direction	Work Function (ev)
A	$1\ \bar{7}\ 10$	4.8
	$\bar{1}\ \bar{1}\ 1$	4.4
	$\bar{10}\ 5\ 7$	4.5
	$\bar{5}\ 1\ 1$	4.3
	$\bar{25}\ \bar{2}\ 1$	4.5
	$\bar{8}\ 1\ \bar{3}$	4.4
	$3\ 1\ \bar{2}$	4.6
	$\bar{5}\ 3\ \bar{5}$	4.4
	$\bar{1}\ 7\ \bar{10}$	4.6
B	$\bar{7}\ \bar{1}\ 7$	4.7
	$\bar{1}\ 1\ 6$	4.3
	$1\ 1\ 2$	4.7
	$3\ 2\ 3$	4.4
	$8\ 4\ 5$	4.7

c. On-axis Molybdenum. Work functions were measured photometrically for several molybdenum single crystals. All of these crystals had surfaces that were accurately in the 110-zone. Values for the various directions of interest are recorded in TABLE 2 for two different crystals. Examination of the crystals with a Unitron metallograph revealed plateau-like structure in all cases on the surfaces normal to the < 110 >, < 112 > and < 001 > directions, while no well-defined structure was found on the surfaces normal to the < 111> and < 116 > directions. Similar to the case of on-axis tungsten, prolonged heating at 1800°K produced work function minima on the low index directions. This type of development as it appears in the photometer scan is shown in Fig. 7 at the < 112 > directions.

TABLE 2

Crystal	Direction	Work Function (ev)
1	110	4.83
2		4.81
1	112	4.69
2		4.72
1	100	4.57
2		
1	111	4.40
2		4.42
1	116	4.31
2		4.33

Note: The low index directions are in error as in the case of W, because of elastically scattered electrons.

2. Average Emission Constants.

Making use of the diode characteristics of the projection diode, Richardson lines such as that illustrated in Fig. 2 were obtained for monocrystalline tungsten and molybdenum filaments. In this case the various crystallographic areas served as patches exposed to a common collector. The average constants ϕ_R and A_R are tabulated in TABLE 3, together with the usual values for polycrystalline filaments.

TABLE 3

Emitter Type	Material	ϕ_R	A_R
Monocrystalline	tungsten	4.41	40.3
	molybdenum	4.40	40.0
Polycrystalline	tungsten	4.54	60-70
	molybdenum	4.36	60-70

E. The Scattering Correction

The experimental method and results for the measurement of elastically scattered electrons, which are the main source of error for work function determination in the low index directions for single crystal filaments, is discussed in reference 10; a complete account will be obtainable in an Air Force Scientific Report, now in preparation. The main results are these: (1) scattering percentages as high as 6.2 were measured for the projection diode described in Section C. (2) Calculations indicate that at least 65% of the emission current measured in the < 110 > can be spurious due to this cause. (3) Although slightly low compared with reported values, the order of magnitude and sign of the temperature coefficient of work function reported for the various crystallographic directions on tungsten[11] may be accounted for by this spurious effect.

F. Discussion and Conclusions.

1. Work Functions. TABLE 2, Section B, together with TABLE 1,

reference 10, indicate quite clearly that there is a one-to-one relationship between the crystallographic work functions of molybdenum and those of tungsten. This reflects the influence of surface structure on work function; the two refractory metals have almost identical crystal structures, and although the annealing temperatures are different for the two filaments, the surface modifications produced on equilibration appear the same. It is also of interest that the photometer traces for W and Mo recrystallized filaments are identical, indicating similarity of patch structure for each emitter as a whole. This leads to a measured identical average work function of about 4.4 ev and an A-value of 40 for both metals given in TABLE 3; thus work functions of 4.54 ev for W and 4.36 ev for Mo usually measured for these materials are strongly influenced by the patchiness of the polycrystalline specimens employed. The results of TABLE 1, which gives the point-by-point work functions for the off-axis tungsten crystals, would seem to emphasize that micropatch structure may contribute an important part to the work function. These data show that the work function values assigned to the various low index directions for tungsten may be obtained when the surface of the recrystallized filament is not in the 110-zone. In fact, when the correction for elastically scattered electrons is carried out higher work function surfaces of greater thermal stability may be found to exist on surfaces of recrystallized W and Mo filaments with the wire axis slightly deviated from the < 110 > direction.

In view of the above results, it would also seem to follow that the large difference in average work functions usually found for molybdenum[12] in wire and sheet form can be attributed to the patch effect resulting from different types of grain growth in the two forms.

2. Surface Equilibration and Faceting. Recrystallized tungsten or molybdenum filaments require long periods of annealing at elevated temperatures to bring the point-by-point work functions to stationary values. The temperatures used in this work were 2300°K for tungsten and 1800°K for molybdenum. Metallographic examination reveals a correlation between these equilibrated surfaces and work function: (a) the areas associated with high work function are faceted, and (b) no faceting occurs on the areas associated with low work functions. (See Fig. 20, reference 10, pg. 21a). This association applies to the off-axis crystals of tungsten described in Section D 1a as well as to those having surfaces in the 110-zone. It is usual in tungsten[1] and often in molybdenum, for faceted areas to have shingles or plateaus with steps of 10,000 or more angstroms. These plateaus also appeared on the facets of high work function for the off-axis tungsten crystals.[13] Quite often in the case of both W and Mo crystals grown by the torsion technique, an emission maximum develops at the center of the high work function facet as a result of further heat treatment (See Fig. 7), and this mode always correlates with the absence of shingles on the faceted area. It also appears from the metallography that at this stage the center of the faceted area is no longer smooth and flat (see Fig. 22, reference 10, pg. 21a).

These data seem to indicate that a smooth faceted area on a recrystallized filament is not a form of high thermal stability, and that a more stable state is arrived at when a fine thermal etch develops in the middle of the facet, or by the formation of plateaus. The first condition seems more probable when the crystal surfaces are accurately

located in the 110-zone, while the second occurs when these planes are slightly tilted. Although the highest measured work function reported[14] for metals is on a field-desorbed tungsten point for the < 110 > direction, the largest values measured thermionically have not been reported for smooth surfaces.[15]

Except for the facets and shingles, no other well-defined surface structure was found on the recrystallized filaments, but the severe heat treatment needed for equilibration always change the surface from an initially smooth polished appearance to one with many crevices, "lakes," pits and other defects which apparently have no correlation with the thermionic emission.

G. Contract Reports.

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R. Anthony, F. Gardner, and E. Coomes, "Thermionic Emission from a Single Crystal Tungsten Wire with 110 Inclined to Wire Axis," Bull. Am. Phys. Soc. 6, 422 (1961).

F. Gradner, F. Girouard, R. Anthony, and E. Coomes, "A Projection Diode Technique for the Thermionic Emission from Single Crystals of Refractory Metals," AFCRL-64-234, Scientific Report No. 1, Contract No. AF 19(604)-8434, 8 January 1964.

H. Contract Personnel.

1. Staff: E. A. Coomes and R. L. Anthony

2. Graduate Students: F. Gardner, F. Girouard, J. Lauffenburger, W. Boeck, and I. D'Haenens.

3. Technicians: E. Parsons and N. Nash.

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10. F. Gardner, F. Girouard, R. Anthony, and E. Coomes, Scientific Report No. 1, AFCRL-64-234 , 8 January 1964.
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12. R. C. Jaklevic and D. W. Juenker, J. Appl. Phys. 33 , 562 (1962).
13. F. Gardner, F. Girouard, R. Anthony, and E. Coomes, AFCRL-64-234, Scientific Report No. 1, Contract No. AF 19(604)-8434, 8 January 1964.
14. R. D. Young and E. W. Müller, J. Appl. Phys. 33 , 91 (1962).
15. F. L. Hughes, H. Levinstein, and R. Koplan, Phys. Rev. 113 , 1023 (1959(.

FIGURES

FIGURE 1

The Projection-diode Tube

A. Collector

B. Pyrex tube wall

C. Stannic chloride conducting coating

D. Phosphor

E. Aluminum film

F. Recrystallized emitter filament

F_1 Molybdenum getter filament

G_1, G_2 Stannic chloride guard rings

S. Zigzag molybdenum spring

S - S' Section through tube wall and screen

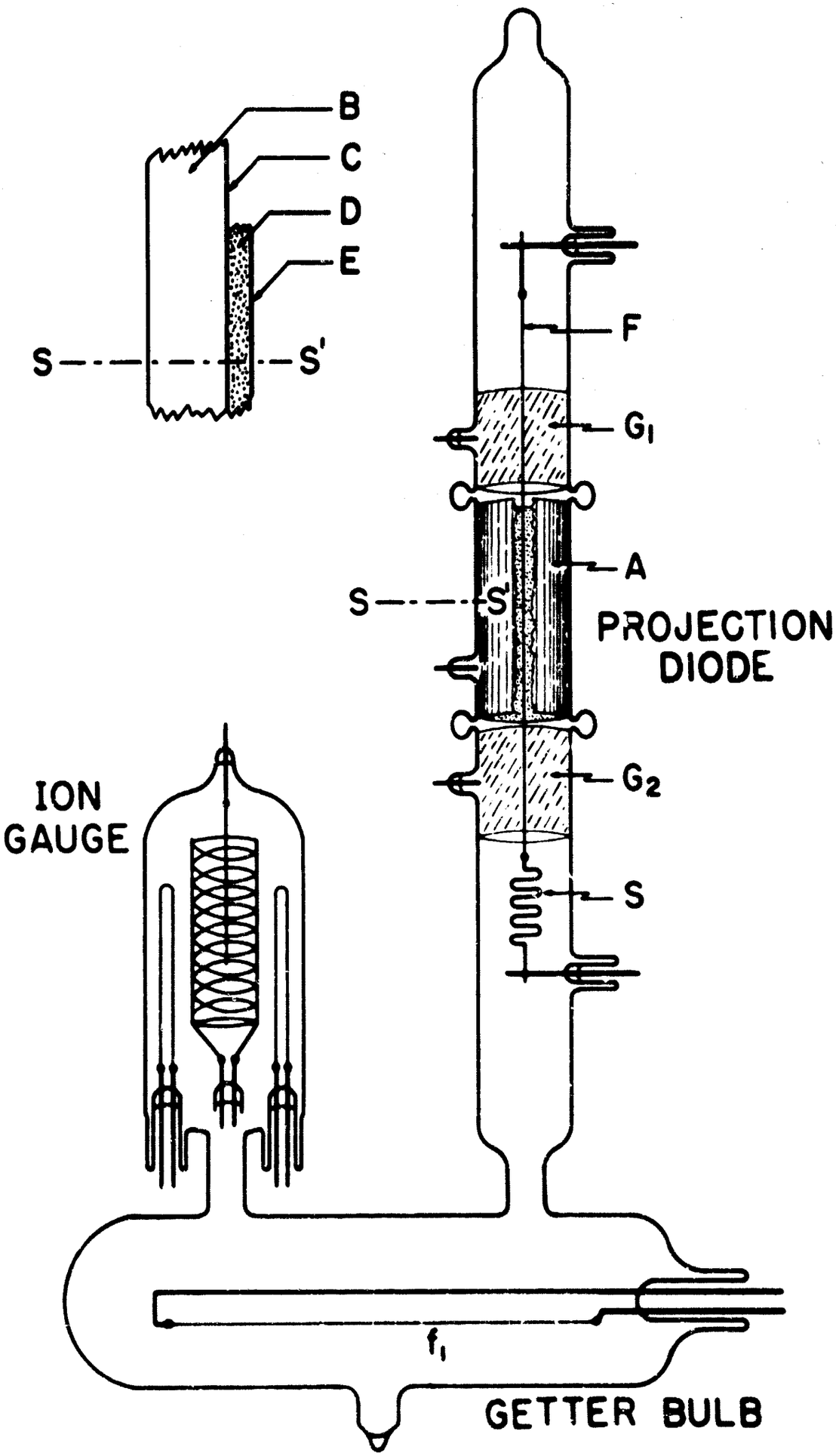

B
C
D
E
S
S'
F
G1
A
S
S'
PROJECTION
DIODE
G2
S
ION
GAUGE
f1
GETTER BULB

FIGURE 2

Richardson plot for a recrystallized molybdenum filament, taken with projection diode used as a diode. The section of filament enclosed by the collector A contained four adjacent single crystals.

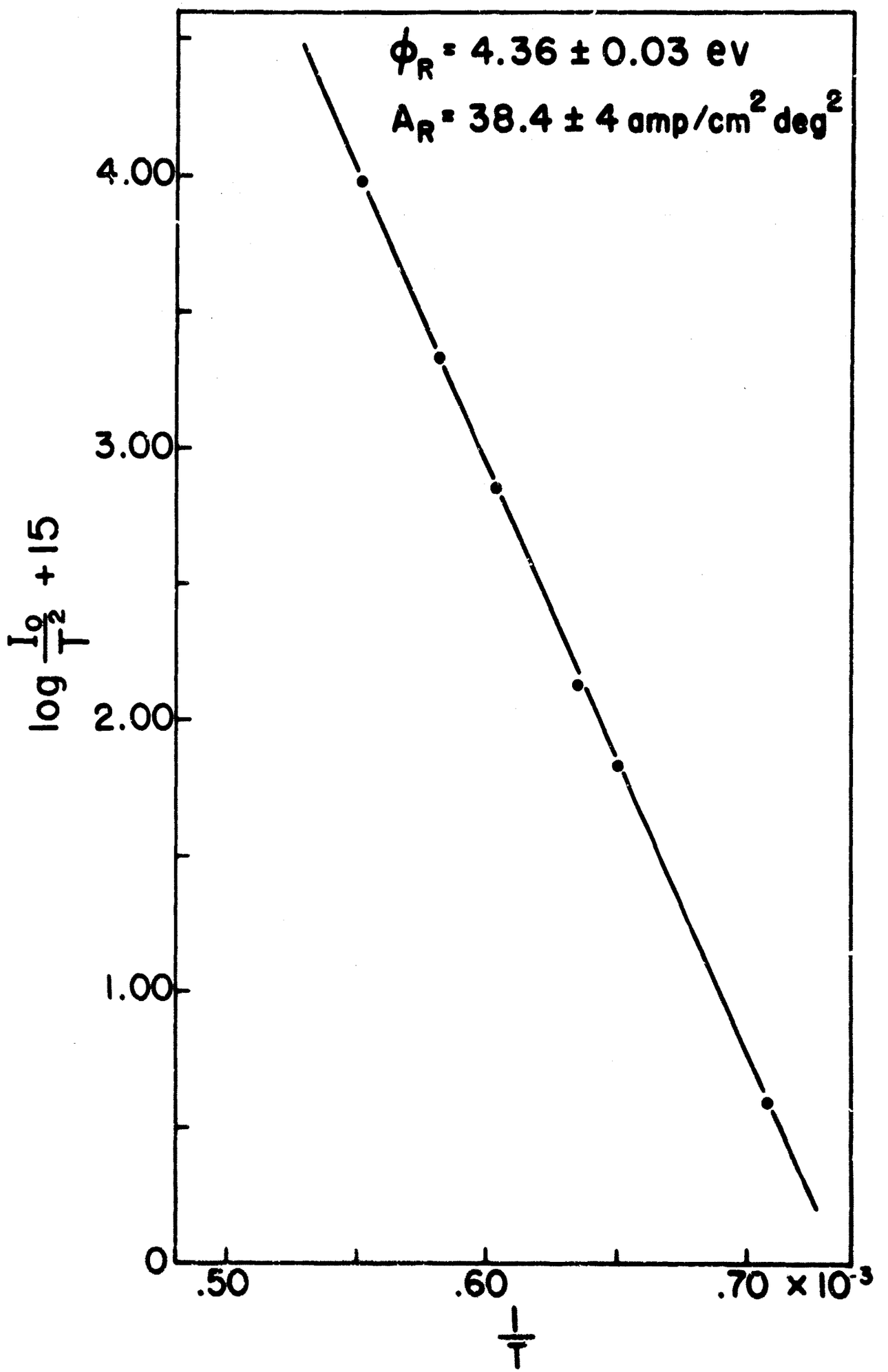

$\phi_R = 4.36 \pm 0.03$ ev
$A_R = 38.4 \pm 4$ amp/cm^2 deg^2
4.00
3.00
2.00
1.00
0
$\log \frac{I_0}{T^2} + 15$
.50
.60
.70 x 10^{-3}
$\frac{1}{T}$

FIGURE 3

Photometric scan of the projection diode for one of the molybdenum crystals contained within the collector. This represents the emission vs orientation; the symmetry gives evidence that the surface of the recrystallized filament is probably in the 110-zone.

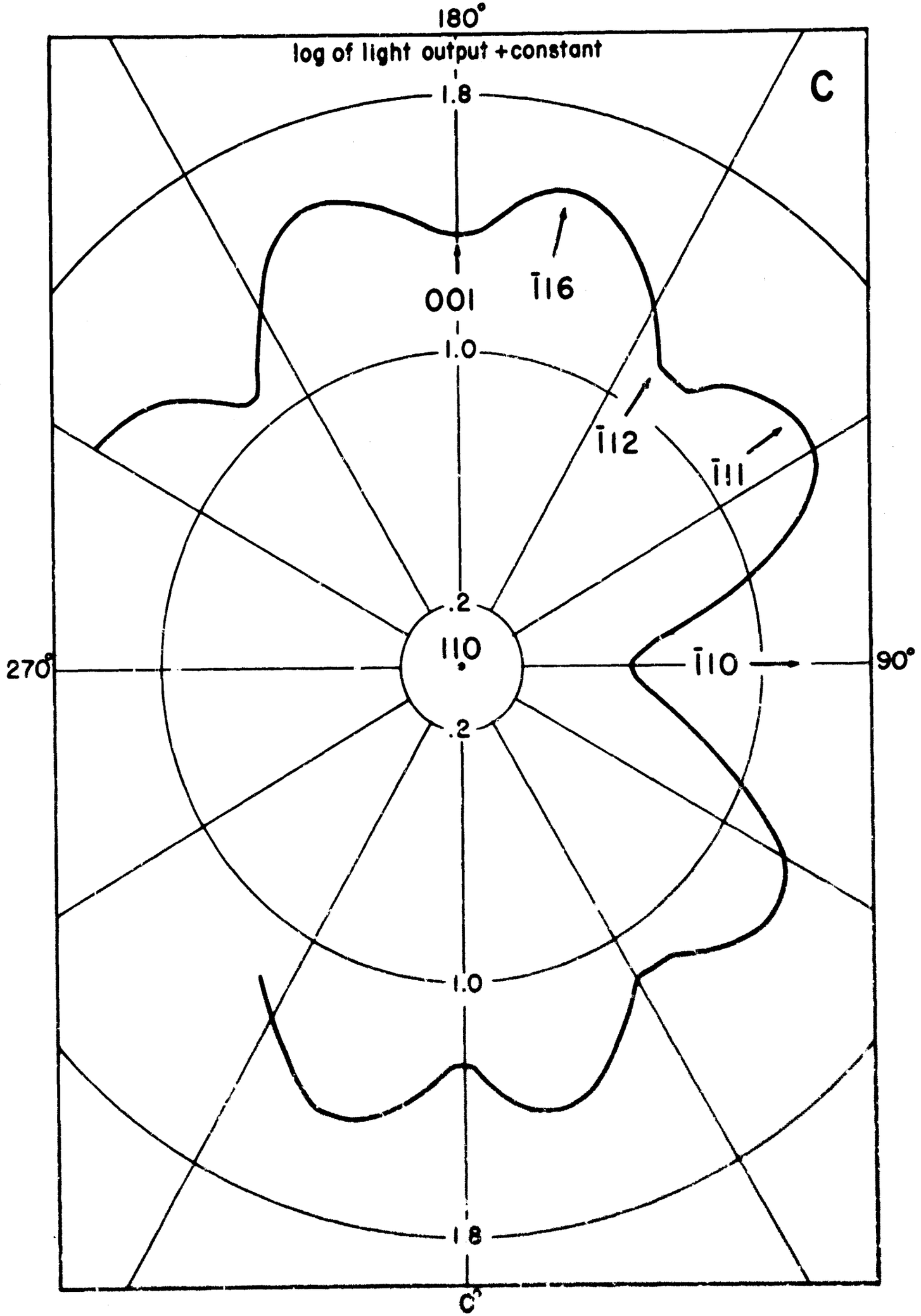

180°
log of light output +constant
C
1.8
001
$\bar{1}16$
1.0
$\bar{1}12$
$\bar{1}11$
.2
110
270°
$\bar{1}10$
90°
.2
1.0
1.8
C

FIGURE 4

Point-by-point Richardson plots taken photometrically at the extreme of the scan in Fig. 3. B is the light output from the projection diode screen as read by the photomultiplier photometer, and E is the field applied to the filament. Work functions for molybdenum derived from the slopes of the Richardson lines are recorded.

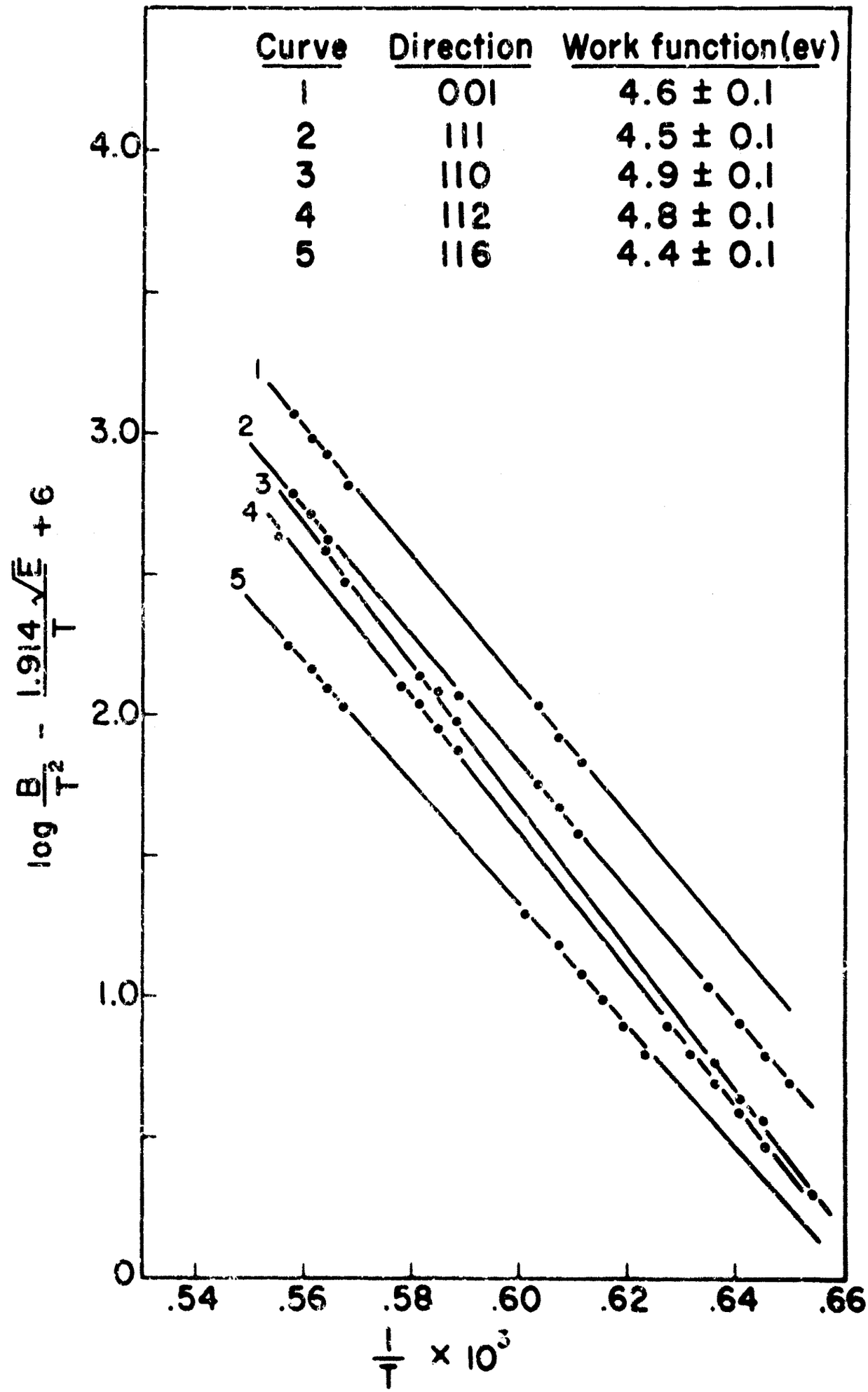

Curve Direction Work function(ev)
1 001 4.6 ± 0.1
2 111 4.5 ± 0.1
3 110 4.9 ± 0.1
4 112 4.8 ± 0.1
5 116 4.4 ± 0.1
4.0
3.0
2.0
1.0
0
1
2
3
4
5
log B/T² - 1.914√E/T + 6
.54
.56
.58
.60
.62
.64
.66
1/T × 10³

FIGURE 5

Photometric scan for off-axis single tungsten crystal A. See text, page 6, for meaning of notations.

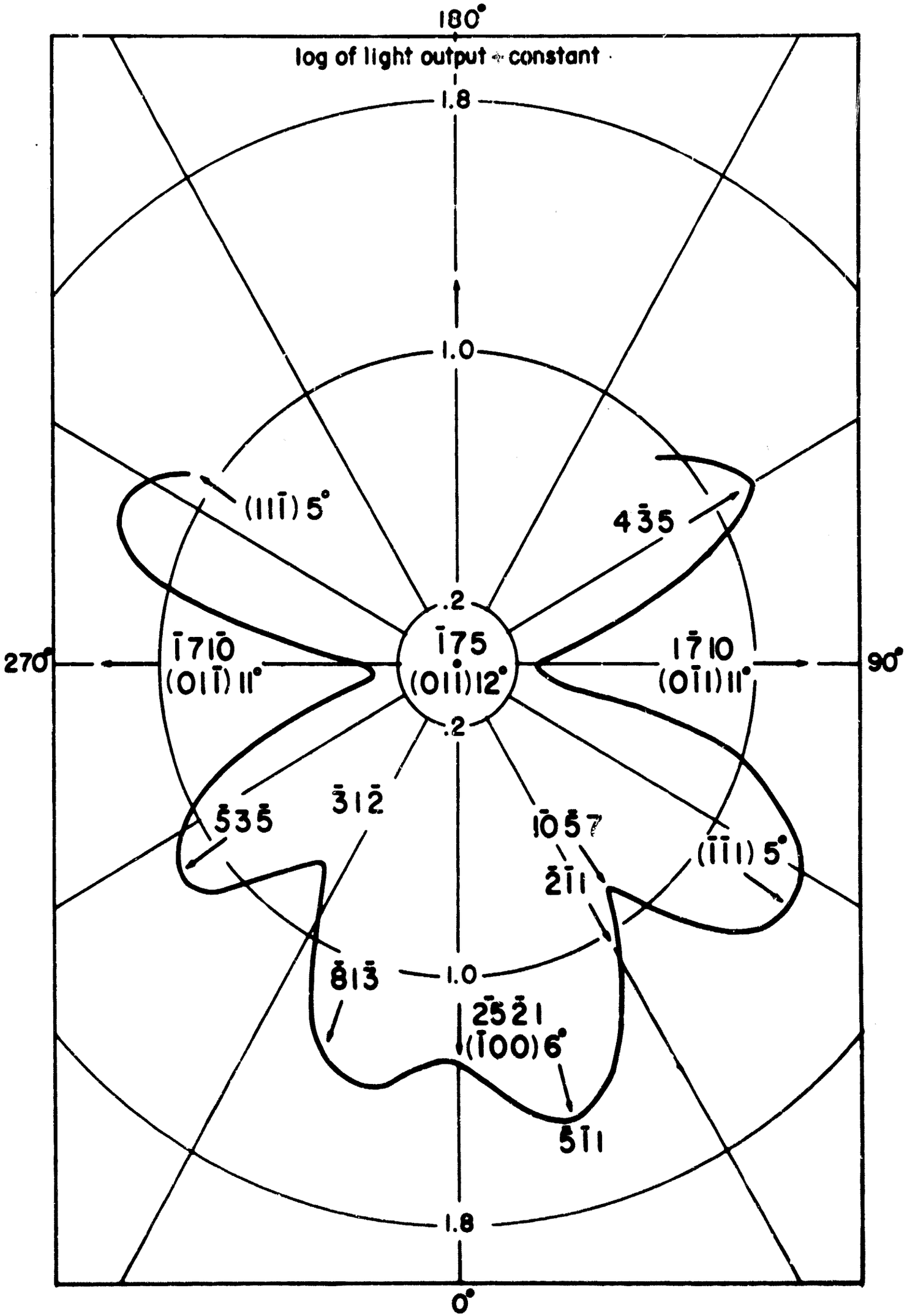

180°
log of light output + constant
1.8
1.0
.2
.2
1.0
1.8
0°
270°
90°
(111) 5°
4 3 5
1 7 1 0
(0 1 1) 11°
1 7 5
(0 1 1) 12°
1 7 1 0
(0 1 1) 11°
5 3 5
3 1 2
1 0 5 7
(1 1 1) 5°
2 1 1
8 1 3
2 5 2 1
(1 0 0) 6°
5 1 1

FIGURE 6

Photometric scan for off-axis tungsten crystal

B. See text, page 6, for meaning of notations.

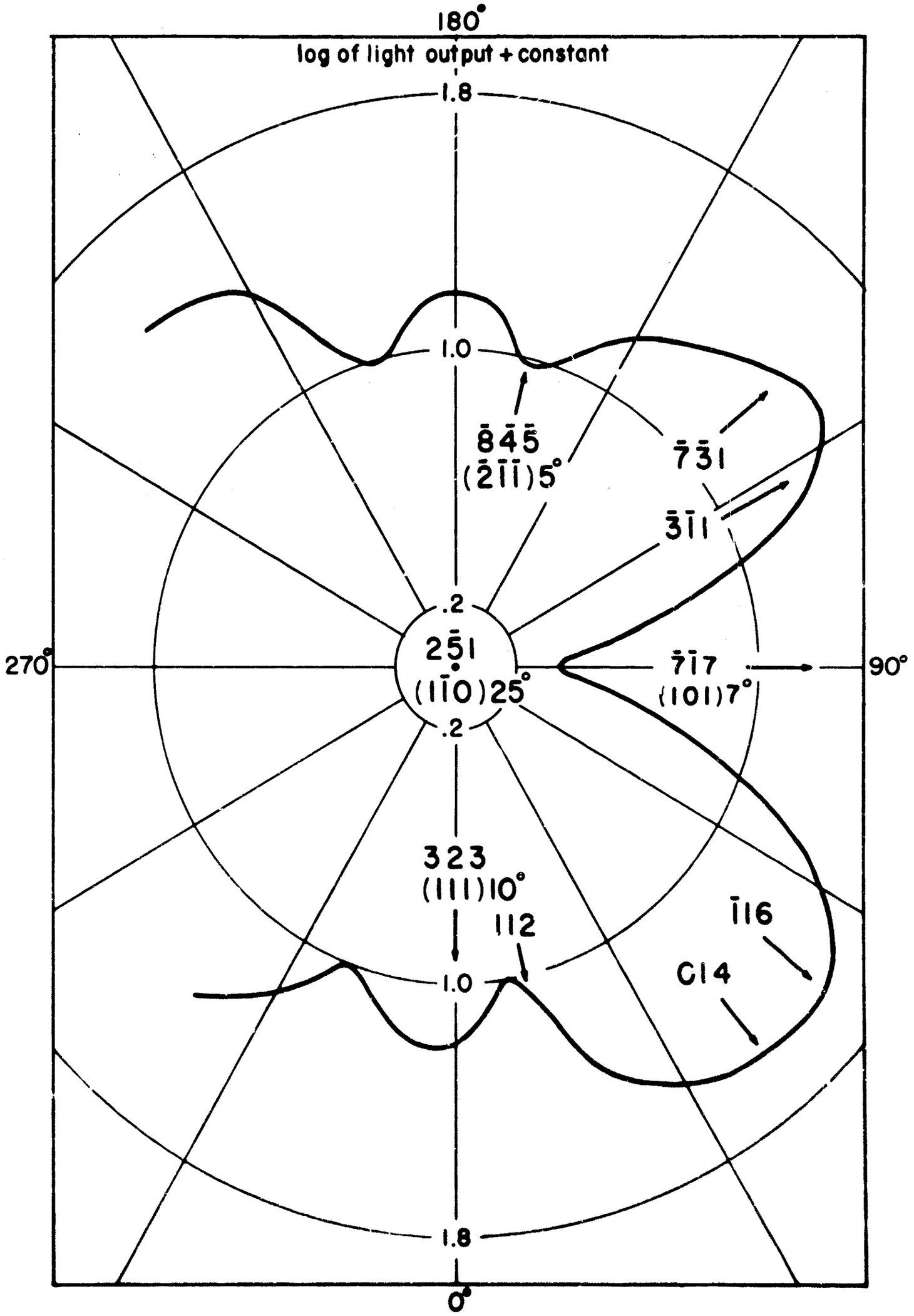
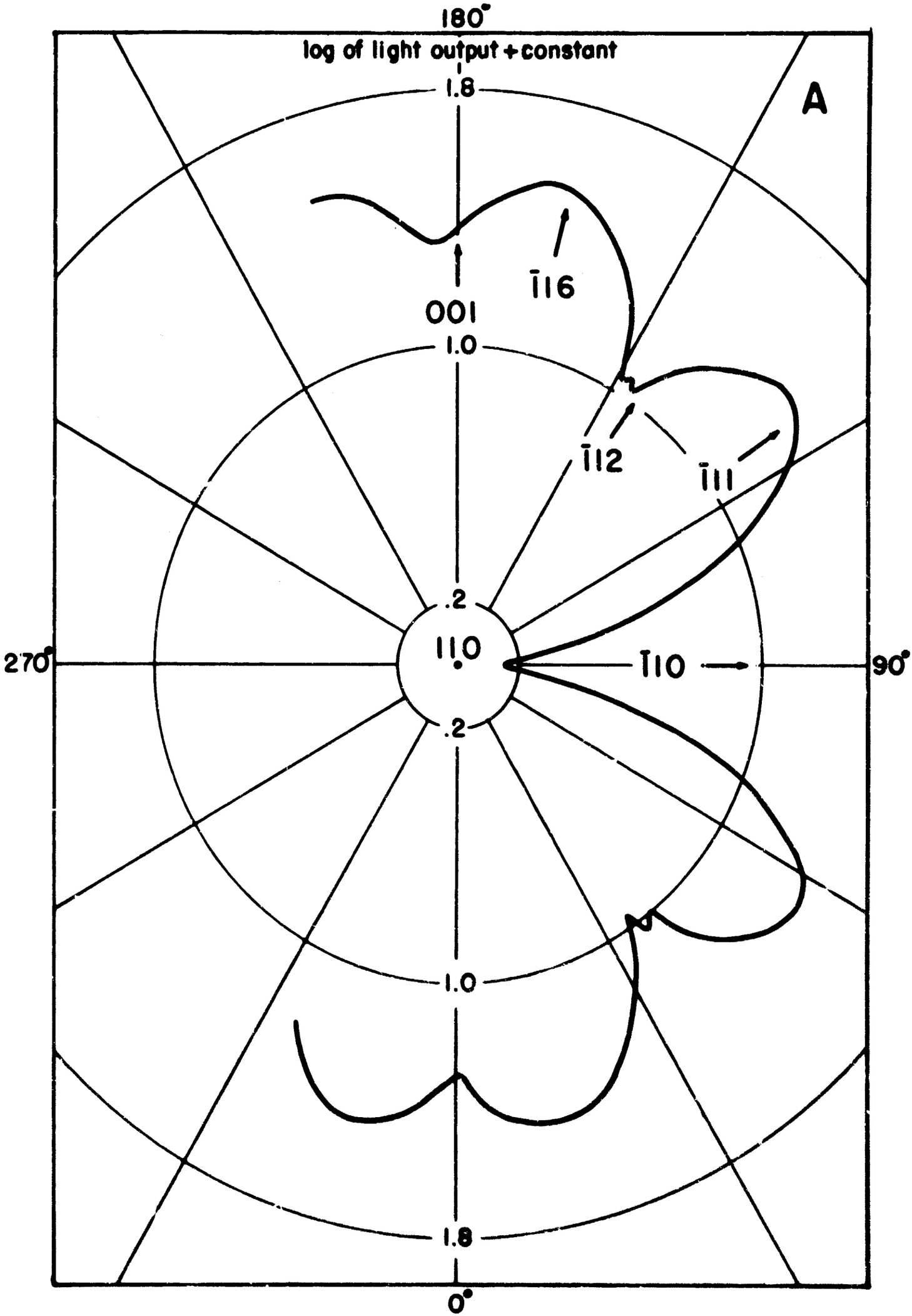

180°
log of light output + constant
1.8
1.0
.2
270°
90°
.2
1.0
1.8
0°
8 4 5
(2 1 1)5°
7 3 1
3 1 1
2 5 1
(1 1 0)25°
7 1 7
(1 0 1)7°
3 2 3
(1 1 1)10°
1 1 2
1 1 6
C 1 4

FIGURE 7

Photometric scan for an on-axis molybdenum single crystal, showing decrease of work function in the < 211 > directions, following heat treatment at 1800°K.


180°
log of light output + constant
1.8
A
001
$\bar{1}16$
1.0
$\bar{1}12$
$\bar{1}11$
.2
270°
110
$\bar{1}10$
90°
.2
1.0
1.8
0°